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14. ABSTRACT Attempts were made to develop liquid crystals based on the Pd/Cu-mediated cyclization of o-iodo-trimethylethynylbenzenes. We found that the palladation of the triazene protected intermediate led to a stable organo-palladium complex, frustrating further reaction. An alternative route, using the dehydrofluorination of triazene functional trifluorostyrenes led to the desired building block. Unfortunately, cyclization proved unsuccessful.					
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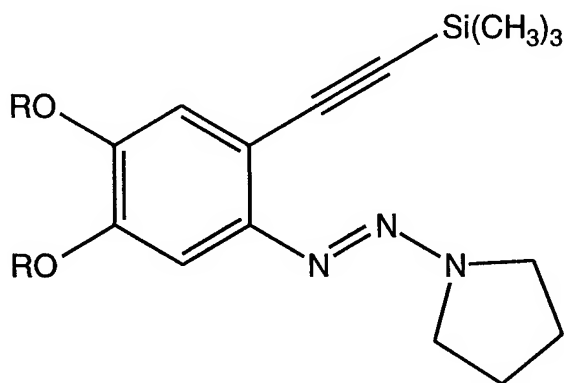
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Final Technical Report

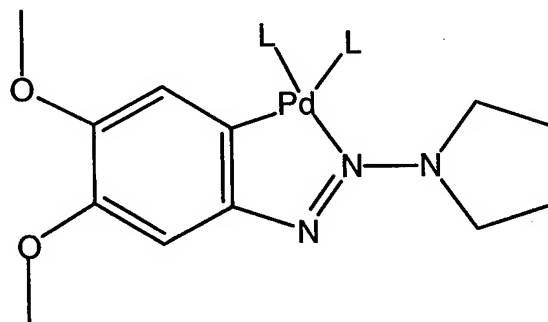
This work represents the doctoral dissertation of Dr. Andre' A. Jones.

The overall goal was to develop a reproducible route to the double protected monomer and its Pd/Cu catalyzed trimerization.

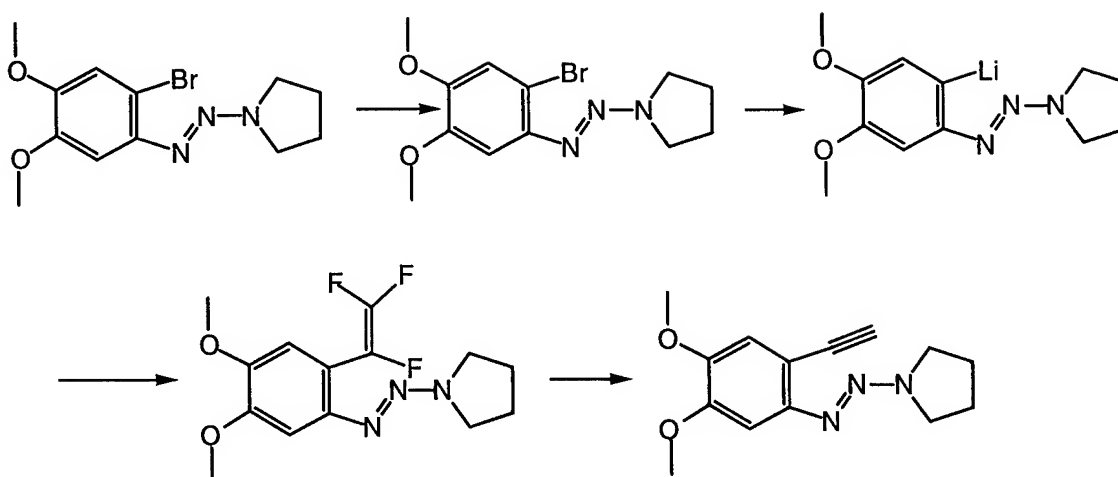


We start with 4-bromocatechol, convert this to the dialkyl ether, nitrate at the 5-position with nitric acid/acetic acid (this to avoid multiple nitration), reduce the nitro group to the amine via catalytic hydrogenation over platinum on charcoal at 3 atmospheres and room temperature, diazotize and react with a cyclic amine to afford the 1-bromo-2-(3,3-teramethylenetriazo)-4,5-dialkoxy-benzene. Attempts to react this material with trimethylsilylacetylene under Heck reaction conditions [Cu(I)/Pd(0)/triethylamine/tetrakis(triphenylphosphine)] afforded a brown oil with little indication of reaction. It was assumed that the bromo-derivative with the dialkoxy substituents was too unreactive under these conditions. Therefore, we synthesized 1-tributylstanyl-2-trimethylsilyl-ethyne and used Stille coupling conditions to convert the bromine to an acetylenic unit. To improve the reaction rate, tri-2-furyl-phosphine was synthesized and used in place of triphenyl phosphine and the dibenzalacetone (dba) derivatives of palladium used in lieu of tetrakis(triphenylphosphine)palladium

as the phosphine ligand. The stannyl-silyl acetylene proved unstable under the reaction conditions, losing the silyl group and dimerizing to form the distannyl diacetylene. We then attempted the same reaction with 1-tributylstanyl ethyne. This proved successful, but very slow. Reactions were complete in 12 days. Because these coupling reactions are prone to side reaction such as oxidative coupling, we again explored the Heck reaction for the coupling of the bromo-triazene with trimethylsilylacetylene, using the new catalyst system (rather than the commercial tetrakis(triphenyl)phosphine palladium). Again, we were unable to observe coupling. We ultimately attributed this problem to the formation of a pallacycle with structure



To circumvent this problem, a new approach was undertaken. Starting with the bromo-triazene, the system was metallated, reacted with chlorotrifluoroethylene, and then through reductive elimination, the desired acetylene formed.



A crystal structure corroborated this structure as well as that of the trimethylsilyl protected derivative. However, cyclization of this materials proved ineffective. Based on other work and some "personnel" related issues, this may have been due to an "operator" problem. However, the funding and time for the program ran out at this stage and further reactions we not pursued.

Dr. Dirk Singer, an expert in the field of discotic liquid crystal synthesis and characterization, joined the group in July of 1996 and focused his initial efforts in synthesis of model compounds such as hexakis(pentylthio)triphenylene and hexakis(pentyloxy)triphenylene. He is also developed a model for core/core interactions in discotic liquid crystals utilizing *ab initio* molecular orbital theory. These studies include interaction between electron donor discotics and electron acceptors, such as trinitrofluorenone. Initial results indicate that the models give a good match for equilibrium inter-core distance based on diffraction studies. A potential energy function for incorporation into molecular dynamics and mechanics studies was developed